I CLAIM:

A method of speciated isotope dilution measurement of a sample comprising

providing at least one predetermined stable isotope,

speciated enriched isotope corresponding to the species to be measured in said sample, spiking the sample containing said specie to be measured,

equilibriating said isotopic spiked species with said species to be

measured,

separating at least a portion of said species from said sample, making isotope ratio determinations for each said specie to be measured and mathematically deconvoluting said species concentration while correcting for species conversion, and

effecting said mathematical deconvolution while correcting for incomplete separation of said species from said sample.

The method of speciated isotope dilution measurement of claim
 including
 employing said method on more than one said species to be

3. The method of speciated isotope dilution measurement of claim 2 including

employing said method in quantifying Cr(III) and Cr(VI).

4. The method of speciated isotope dilution measurement of claim

2 including

effecting said mathematical deconvolution employing the

following formulas:

measured simultaneously.

$$R_{50/52}^{III} = \frac{(^{50}A_xC_x^{II}W_x + ^{50}A_s^{III}C_s^{III}W_s^{III})(1-\alpha) + (^{50}A_xC_x^{VI}W_x + ^{50}A_s^{VI}C_s^{VI}W_s^{VI})\beta}{(^{52}A_xC_x^{III}W_x + ^{52}A_s^{III}C_s^{III}W_s^{III})(1-\alpha) + (^{52}A_xC_x^{VI}W_x + ^{52}A_s^{VI}C_s^{VI}W_s^{VI})\beta}$$

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$$R_{53/52}^{III} = \frac{(^{53}A_{x}C_{x}^{III}W_{x}^{I} + ^{53}A_{s}^{III}C_{s}^{III}W_{s}^{III})(1-\alpha) + (^{53}A_{x}C_{x}^{VI}W_{x} + ^{53}A_{s}^{VI}C_{s}^{VI}W_{s}^{VI})\beta}{(^{52}A_{x}C_{x}^{III}W_{x} + ^{52}A_{s}^{III}C_{s}^{III}W_{s}^{III})(1-\alpha) + (^{52}A_{x}C_{x}^{VI}W_{x} + ^{52}A_{s}^{VI}C_{s}^{VI}W_{s}^{VI})\beta}$$

$$R_{50/52}^{VI} = \frac{(^{50}A_{x}C_{x}^{III}W_{x} + ^{50}A_{s}^{III}C_{s}^{III}W_{s}^{III})\alpha + (^{50}A_{x}C_{x}^{VI}W_{x} + ^{50}A_{s}^{VI}C_{s}^{VI}W_{s}^{III})(1-\beta)}{(^{52}A_{x}C_{x}^{III}W_{x} + ^{52}A_{s}^{III}C_{s}^{III}W_{s}^{III})\alpha + (^{52}A_{x}C_{x}^{VI}W_{x} + ^{52}A_{s}^{VI}C_{s}^{VI}W_{s}^{VI})(1-\beta)}$$

$$R_{53/52}^{VI} = \frac{(^{53}A_{x}C_{x}^{III}W_{x} + ^{53}A_{s}^{III}C_{s}^{III}W_{s}^{III})\alpha + (^{53}A_{x}C_{x}^{VI}W_{x} + ^{53}A_{s}^{VI}C_{s}^{VI}W_{s}^{III})(1-\beta)}{(^{52}A_{x}C_{x}^{III}W_{x} + ^{52}A_{s}^{III}C_{s}^{III}W_{s}^{III})\alpha + (^{52}A_{x}C_{x}^{VI}W_{x} + ^{52}A_{s}^{VI}C_{s}^{VI}W_{s}^{VI})(1-\beta)}$$

where,

 $R_{50/52}^{III}$  is the measured isotope ratio of  $^{50}$ Cr to  $^{52}$ Cr of Cr(III) in the spiked sample

 $^{50}A_x$  is the natural atomic fraction of  $^{50}Cr$  in the sample

 $C_x^{\text{III}}$  is the concentration of Cr(III) in the sample ( $\mu$ mole/g, unknown)

W<sub>x</sub> is the weight of the sample in grams

<sup>50</sup>A<sub>s</sub><sup>III</sup> is the atomic fraction of <sup>50</sup>Cr in the isotopic spike: <sup>50</sup>Cr(III)

 $C_s^{III}$  is the concentration of Cr(III) in the  $^{50}$ Cr(III) spike ( $\mu$ mole/g)

W<sub>s</sub> is the weight of the <sup>50</sup>Cr(III) spike in grams

 $C_x^{VI}$  is the concentration of Cr(VI) in the sample ( $\mu$ mole/g, unknown)

 $\alpha$  is the percentage of Cr(III) oxidized to Cr(VI) after spiking (unknown)

B is the percentage of Cr(VI) reduced to Cr(III) after spiking (unknown)

5. The method of speciated isotope dilution measurement of claim
1 including
employing a mass spectrometer to determine said isotopic
element ratios.

6. The method of speciated isotope dilution measurement of claim 1 including

tagging said enriched isotope with an isotopic tag in the same speciated form as the species to be measured.

- 7. The method of speciated isotope dilution measurement of claim
  1 including
  employing time resolution chromatography to effect said
  separation.
- 8. The method of speciated isotope dilution measurement of claim

  1 including

  employing said process on a sample which has experienced specie conversion prior to separation.
- 9. The method of speciated isotope dilution measurement of claim 1 including effecting said equilibrium in an aqueous solution.
  - 10. The method of speciated isotope dilution measurement of claim employing said process on an incompletely separated specie.
- 11. The method of speciated isotope dilution measurement of claim 3 including
  effecting said separation after reduction of a substantial portion of Cr(VI) to Cr(III).
- 12. The method of speciated isotope dilution measurement of claim 1 including employing said process on a soil sample.
- 13. The method of speciated isotope dilution measurement of claim 1 including employing said process on an aqueous sample.
- 14. The method of speciated isotope dilution measurement of claim
  1 including
  employing said process on solid waste from a chromite ore
  processing system.
- 15. The method of speciated isotope dilution measurement of claim
  1 including
  storing said sample after said equilibrating step and prior to said separating step.

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1 including

- 16. The method of speciated isotope dilution measurement of claim 1 including effecting said mathematical deconvoluting simultaneously with respect to more than one species to be measured.
- 17. The method of speciated isotope dilution measurement of claim
  16 including
  effecting said mathematical deconvoluting for each species
  independently of other species.
- 1 including
  effecting said mathematical deconvoluting with respect solely to one species to be measured.

The method of speciated isotope dilution measurement of claim

effecting said separation of at least about 5 to 10 percent, but less than 100 percent of each said species from said sample and from said other species before effecting said deconvolution.

19.

20. The method of speciated isotope dilution measurement of claim

1 including

effecting said separation by at least one method selected from

the group consisting of chromatography, microwave assisted extraction, soxhilate extraction, solvent dissolution, acid dissolution, acid or base hydrolysis distillation, centrifugation, and solvent extraction.

- 21. The method of speciated isotope dilution measurement of claim 1 including effecting said separating by microwave assisted extraction for a
- effecting said separating by microwave assisted extraction for a period of about 5 to 15 minutes.
- 22. The method of speciated isotope dilution measurement of claim 21 including effecting said separating at about 90°C to 150°C.
- 23. The method of speciated isotope dilution measurement of claim 1 including



after effecting said speciated isotope dilution measurement of a sample comparing the results of said measurement with measurements made by another type of test to evaluate the validity of said another type of test.

- 24. The method of speciated isotope dilution measurement of claim 23 including
- effecting a plurality of measurements by said another test and effecting said comparison in evaluating the validity of said another type of test.
- 25. The method of speciated isotope dilution measurement of claim 1 including employing said method to prepare speciated spiked standard materials.
- 26. The method of speciated isotope dilution measurement of claim 1 including employing said method to prepare standard materials.
- 27. The method of speciated isotope dilution measurement of claim
  25 including

  creating said speciated spiked standard by spiking separated
  stable isotopes in speciated form.
- 28. The method of speciated isotope dilution measurement of claim
  26 including
  employing said standard materials after storage.
- 29. The method of speciated isotope dilution measurement of claim
  26 including
  employing said method to correct species shifts in said standard

materials after degradation.

- 30. The method of speciated isotope dilution measurement of claim
  21 including
  employing in said microwave extraction closed vessel microwave extraction.
- The method of speciated isotope dilution measurement of claim 23 including





employing said method to validate said tests which are not independently capable of compensating for incomplete species extraction or species conversion.

32. The method of speciated isotope dilution measurement of claim 1 including

performing said method on a species which due to incomplete separation, loss, conversion or degradation has less than 100 percent of said species separated.

33. The method of speciated isotope dilution measurement of claim 32 including

effecting said separation of at least about 5 to 10 percent of said species.